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The Effect of Fuel Composition on Nitrogen Release During Black Liquor Pyrolysis

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The Effect of Fuel Composition on Nitrogen Release During Black Liquor Pyrolysis.

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SUMMARY

NO_x emissions evolve from the black liquor combustion process from a fuel nitrogen pathway. A large component of the fuel nitrogen in black liquor has been found to be organic in nature. The conversion of the nitrogen species to NO_x was found to be dependent not only on the form of the nitrogen (either straight chain amine or heterocyclic in nature), but also on the chemical composition of the matrix. Differences in the conversion have been found in both model systems and during the pyrolysis of commercial black liquors. The variations in the liquor composition are important to understanding the formation of fuel NO_x during black liquor pyrolysis.

INTRODUCTION

In the pulp and paper industry, wood is chemically and thermally degraded to separate the usable fibers from the strength matrix of the wood. Black liquor is the spent chemical solution which is produced during the pulping of wood by the Kraft process. Its composition is typically 50% organic/50% inorganic. Both energy and pulping chemicals are recovered by firing concentrated black liquor in a chemical recovery boiler. The thermal energy is recovered by steam generation, while the inorganic chemicals (mainly Na₂SO₄, Na₂CO₃, and Na₂S) are recovered from a molten smelt formed at the bottom of the furnace for reuse as pulping chemicals. The recovery of energy and inorganic chemicals from the liquor is crucial for the economic and environmental feasibility of the pulping process.

Optimizing black liquor combustion is essential for maximizing the economic benefit and minimizing the environmental impact of the recovery process. One important environmental factor is NO_x. Currently, reported emissions range from 0-155 ppm NO_x. The black liquor contains about 0.1% N, and a conversion of only 20% could represent the majority of the NO_x observed at the stack.¹ The fuel-nitrogen pathway has been reported to be the dominant source for NO_x generation.² Understanding the chemistry leading to the formation of fuel NO_x emissions during boiler operation is a key step in optimization. This work looks at both the form of nitrogen in black liquor fuel and the effects of fuel composition as they relate to the formation of fuel NO_x during recovery boiler operations.

EXPERIMENTAL AND RESULTS

Liquor Composition. Five commercial Kraft black liquors were used in this study. The liquors were obtained from processes pulping pine, pine/birch blend, eucalyptus, and southern pine. The elemental composition of the liquors was determined and is reported in Table 1. These results are within expected values.

Table 1. Elemental composition of commercial Kraft black liquors reported as weight percent of dry solids.

Element	Commercial Kraft Black Liquor				
	Pine	Pine/Birch	Eucalyptus	Southern Pine I	Southern Pine II
C	35.8	33.1	37.3	34.3	31.0
H	3.6	3.4	3.6	3.4	4.1
N	0.06	0.07	0.09	0.06	0.06
S	4.6	5.0	3.4	5.2	2.4
O	32.6	30.1	33.2	33.4	33.8
Na	21.0	25.9	19.0	19.7	21.2
K	1.8	1.8	1.8	3.0	1.5
Cl	0.5	0.6	1.6	0.9	0.6

Nitrogen Form. The chemical form of nitrogen was determined in the two southern pine liquors for comparison. Nitrate/nitrite analysis, GC-MS, and protein and amino acid assays were done. The composition of the nitrogen structures is indicated in Figure 1.

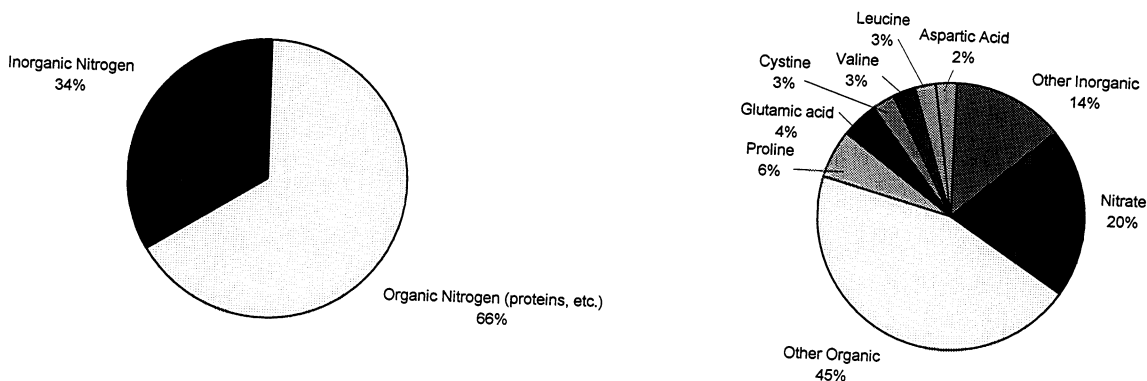


Figure 1. Chemical components representing the total nitrogen fraction of the southern pine I black liquor.

About two-thirds of the southern pine liquor nitrogen composition is made up of protein species such as heterocyclic ring compounds and amino acids. The southern pine I liquor was found to have a free amino acid composition of about 20% of the total nitrogen in the system with proline ($C_5H_9NO_2$) comprising the largest fraction. Glutamic acid ($C_5H_9NO_4$) was present in the largest fraction in the second liquor representing 6% of the total liquor nitrogen. Heterocyclic ring structures, indoles, pyrimidines, and pyrroles, were also observed in the liquors. Similar structures have been noted in other liquors.⁴ The remaining one-third of the nitrogen was assumed to be inorganic. Nitrate was found in fairly high concentrations representing the largest component of the inorganic nitrogen. Other forms of inorganic nitrogen may be present; however, the concentrations of individual species are too low to be detected analytically. Thus, many forms of nitrogen are present in the liquor as a source of fuel nitrogen, and the amounts of individual types of nitrogen are liquor specific.

Fuel Nitrogen Species Conversions. Model fuel nitrogen compounds of those observed in black liquor were combusted in an 1100°C, 75% O_2 environment (ANTEK nitrogen analyzer) to determine the amount of conversion to NO_x under heavily oxidizing

conditions. Results indicated that the conversion of nitrogen to NO_x was found to vary greatly. Conversion of nitrate (R-NO_3), amine (R-NH_3), and heterocyclically bound nitrogen species was low (less than 48%). The exact conversions were highly dependent on the chemical structure. The composition of the matrices in which the nitrogen was bound was also found to be significant. Approximately 0.2 N concentrations of NaOH , Na_2SO_4 , Na_2CO_3 , and Na_2S in solution were evaluated for effects on the conversion of the model fuel nitrogen compounds to NO_x . All species tested were found to reduce the conversion at low nitrogen concentrations (50 ppm). NaOH reduced the conversion the most at a 64% reduction, followed by the Na_2CO_3 and Na_2SO_4 , respectively. As the concentration of nitrogen increased in the samples, the conversions increased; however, the Na_2SO_4 seemed to enhance the conversion at the higher nitrogen concentrations (500 ppm).

Liquor Pyrolysis. Pyrolysis studies were carried out at Åbo Akademi University, Turku, Finland. Individual drops of four of the black liquors weighing from 10-30 mg were pyrolyzed in N_2 . Fixed nitrogen (the sum of NO and the fuel NO_x intermediates, e.g., HCN and NH_3) produced during pyrolysis of two liquors at 100°C intervals and of two liquors at 200°C intervals at temperatures from 300 - 1000°C was measured. The amount of nitrogen released as fixed nitrogen is indicated in Figure 2. Total nitrogen was measured in the remaining char. Results indicated that about 50% of the fuel nitrogen could be volatilized during pyrolysis and 50% remained in the char. Fixed nitrogen represented about 10% of the black liquor nitrogen, while roughly 40% was assumed to be N_2 .

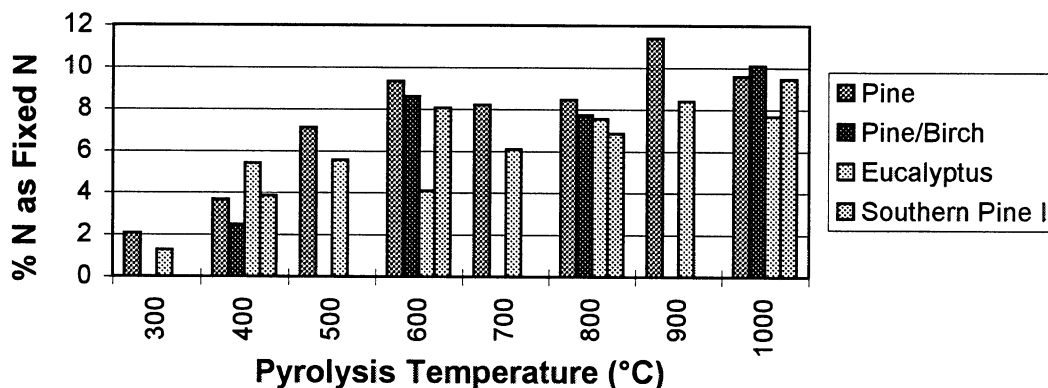


Figure 2. The percent fixed nitrogen (as percent total initial nitrogen) released for liquors pyrolyzed in N_2 at 300 - 1000°C .

DISCUSSION

Black Liquor Nitrogen Species. The nitrogen present in black liquor has been shown to enter the fuel stream from the pulpwood.⁴ Nitrogen has been reported to be present in wood as proteinaceous amino acids and lignin and as nonproteinaceous free amino acids, ureids, alkaloids, and inorganic nitrogen (nitrates and nitrites).⁴ In accordance with previous reports, nitrogen was observed in the liquors as amino acid species and heterocyclic ring forms. Because of the various types of fuel nitrogen species present, more than one pathway may be present for the fuel nitrogen conversion to NO_x .

Nitrogen Conversions. Conversion measurements were made using an ANTEK nitrogen analyzer. This instrument measures total nitrogen using high temperature combustion by converting all forms of nitrogen, except diatomic nitrogen--N₂, to NO and ultimately NO₂ where the relaxation of the latter species is measured using chemiluminescence. When compounds with known nitrogen concentrations are compared to NO, the conversion for that compound can be determined. It was observed that the conversion is affected by the components in the sample matrices that also enter the gas phase upon combustion. Of particular interest for black liquor are the sodium salt species. These species may enter the gas phase forming aerosols which can deposit on the walls of the combustion chamber. The deposits appear to capture a small portion of the nitrogen during repeated measurements. It has been noted that subsequent use of HCl leads to the release of nitrogen. Depletion reactions of NO with sodium salts are currently being investigated.⁵ These *insitu* reactions make the analytical measurement more difficult and can be a significant source of error in nitrogen analysis. Future work will include additional investigations on the capture and release of NO.

Liquor Pyrolysis. The pyrolysis results have been correlated to results published by Aho et al. for similar black liquor pyrolysis conditions.^{6,7} As depicted in Figure 2, the release of nitrogen to form fixed nitrogen species directly during pyrolysis has been shown to increase with temperature up to about 600°C after which it levels off. The release of fixed nitrogen species was found to increase with increasing nitrogen content. This agrees with results from coal pyrolysis studies.⁸ The data for the four liquors are presented for pyrolysis temperatures at 600 and 800°C in Figure 3 along with Aho et al.'s data. The trend observed follows a linear dependence on nitrogen composition.

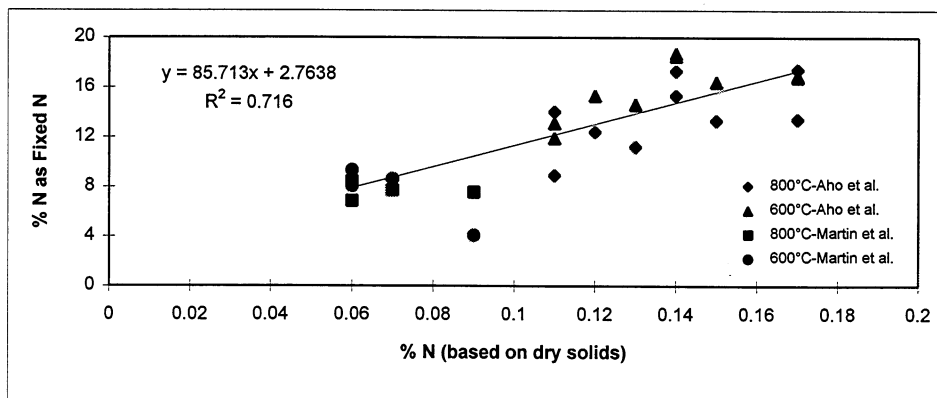


Figure 3. Increasing release of fixed nitrogen with increasing black liquor nitrogen concentration.

Composition Effects. The results of different model nitrogen components have shown that the chemical form of the nitrogen as well as the matrix binding the nitrogen affect the release of the fixed nitrogen species and the ultimate conversion of the fuel nitrogen to NO during pyrolysis. When the composition of the black liquors is considered, trends indicate that the composition of the liquor is also important to the conversion. The data for the percent nitrogen released as fixed nitrogen (i.e., the sum of NO and oxidizable intermediates, HCN and NH₃) are given as a function of the sodium, carbon, and oxygen liquor content with respect to the nitrogen content in Figures 4-6. The data were fitted to second-order polynomial equations with good correlation (R-squared ranged from 0.65-

0.75) for the four independent sets of data shown in each figure. The fit for the data can be improved by combining the two data sets at each temperature.

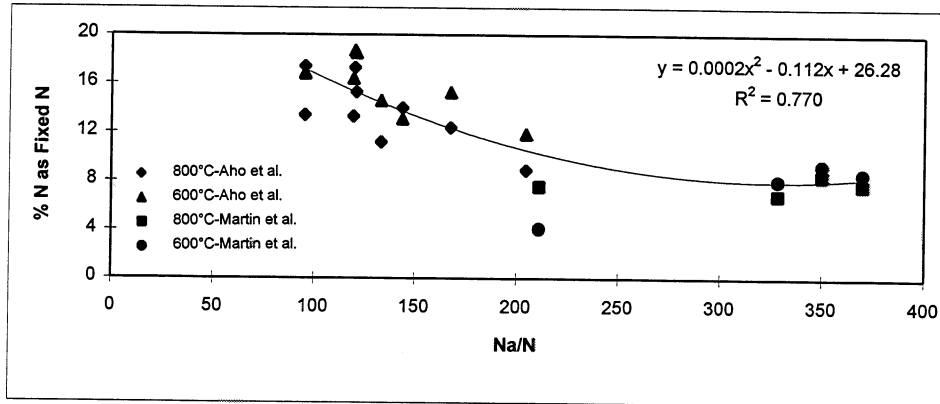


Figure 4. Release of fixed nitrogen with respect to the black liquor sodium/nitrogen concentration.

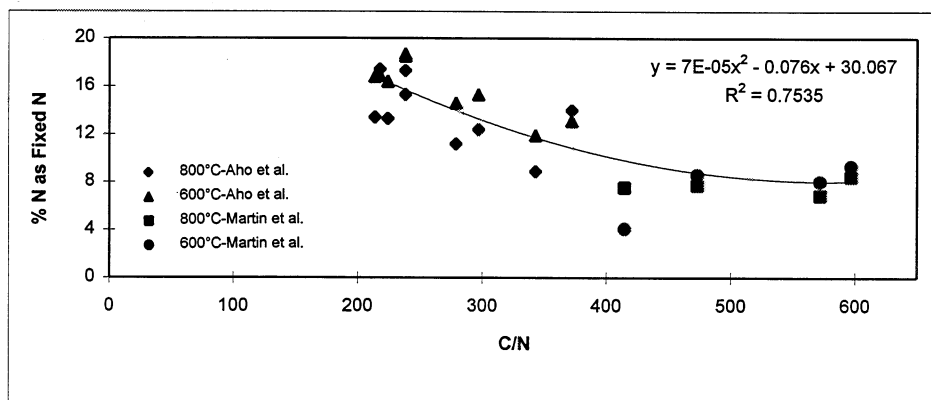


Figure 5. Release of fixed nitrogen with respect to the black liquor carbon/nitrogen concentration.

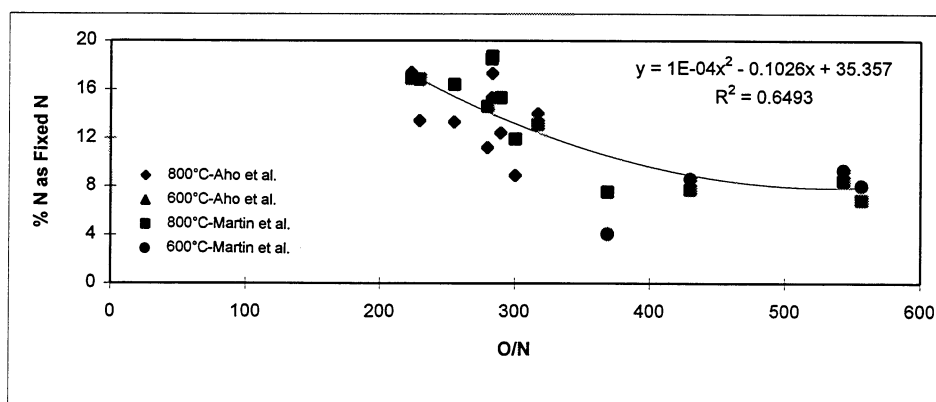


Figure 6. Release of fixed nitrogen with respect to the black liquor oxygen/nitrogen concentration.

All three of the components indicate similar trends for the nitrogen released as fixed nitrogen. Statistical analysis was done to investigate the significance of individual

components. The results indicated the sodium, carbon, and oxygen content of the liquors to be correlated; however, the strongest correlation was observed for the sodium component.

The effects of the composition support the differences in the emission levels observed from various boilers. While operating conditions are known to play a significant role in controlling NO_x emissions,^{9,10} these results also suggest the importance of the liquor composition. Variations in liquor composition appear to be important in understanding the nitrogen release pathways during black liquor pyrolysis.

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LITERATURE CITED

1. Nichols, K.M.; Thompson, L.M.; Empie, H.J., *Tappi Journal*, 76(1):119 (1993).
2. Nichols, K.M.; Lien, S.J., *Tappi Journal*, 76(3):185 (1993).
3. Niemelä, K. "Low-Molecular Weight Organic Compounds in Birch Kraft Black Liquors." Ph.D. Dissertation, University of Helsinki. (1990).
4. Veverka, P.J.; Nichols, K.M.; Horton, R.R.; Adams, T.N., 1993 TAPPI Environmental Conference, TAPPI Press, Atlanta, GA, (1993) p. 777.
5. Thompson, L.M.; Empie, H.J. "Kinetics of NO Depletion by Reaction with Molten Sodium Carbonate." *AIChE Symposium Series #302*, Vol. 90, 1994.
6. Aho, K.; Hupa, M.; Vakkilainen, E., *Tappi Journal*, 77(5):121 (1994).
7. Aho, K.; Hupa, M.; Nikkanen, S., *Tappi Journal*, 77(8):182 (1994).
8. Wendt, J.O.L.; Schulze, O.E., *AIChE Journal*, 22(1):102 (1976).
9. Anderson, P.H.; Jackson, J.C., *Tappi Journal*, 74(1):115 (1991).
10. Feck, R., 1992 TAPPI/CPPA International Chemical Recovery Conference, TAPPI Press, Atlanta, GA. p. 391.

